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Full Paper

## Synthesis and Characterisation of Eight Isomeric Bis(2-pyridyloxy)naphthalenes

Brendan J. O’Keefe and Peter J. Steel\*

Department of Chemistry, College of Science, University of Canterbury, Christchurch, New Zealand.

E-mail: [peter.steel@canterbury.ac.nz](mailto:peter.steel@canterbury.ac.nz)

\* Author to whom correspondence should be addressed.

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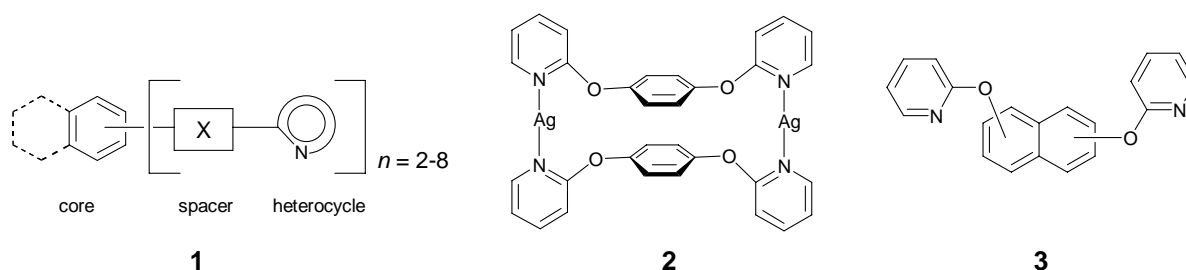
**Abstract:** Eight isomeric bis(2-pyridyloxy)naphthalenes have been prepared from reactions of 2-bromopyridine with the appropriate dihydroxynaphthalene and the products fully characterised by 1- and 2-D NMR spectroscopy.

**Keywords:** N bridging ligands; pyridines; naphthalenes.

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### Introduction

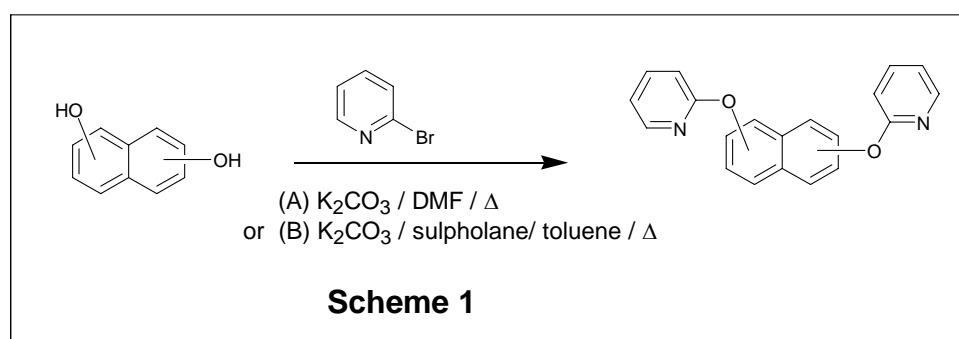
Over the last decade we have reported the synthesis and study of numerous compounds characterised by the schematic representation **1** [1,2]. These are comprised of a central arene core to which are appended a number ( $n$ ) of heterocyclic rings attached via spacer groups (X). Variation of the arene core, the spacer group, the nature of the heterocycle and the number  $n$  has led to an extensive library of bridging ligands that we have used for the construction of a diverse range of 1-, 2- and 3-D metallocyclophane assemblies with various topological architectures. For example, the dimetallocyclophane **2**, stabilised by internal  $\pi$ - $\pi$  stacking of the central benzene rings, was formed by reaction of silver nitrate with 1,4-bis(2-pyridyloxy)benzene, which has a benzene core, an ether oxygen as spacer and ( $n = 2$ ) 2-substituted pyridines as the appended heterocycles [3]. The analogous 3-pyridyl ligand provided access to the first quadruply stranded helicate [4], whereas the 1,2- and 1,3-disubstituted analogues led to a range of other interesting assemblies [5].



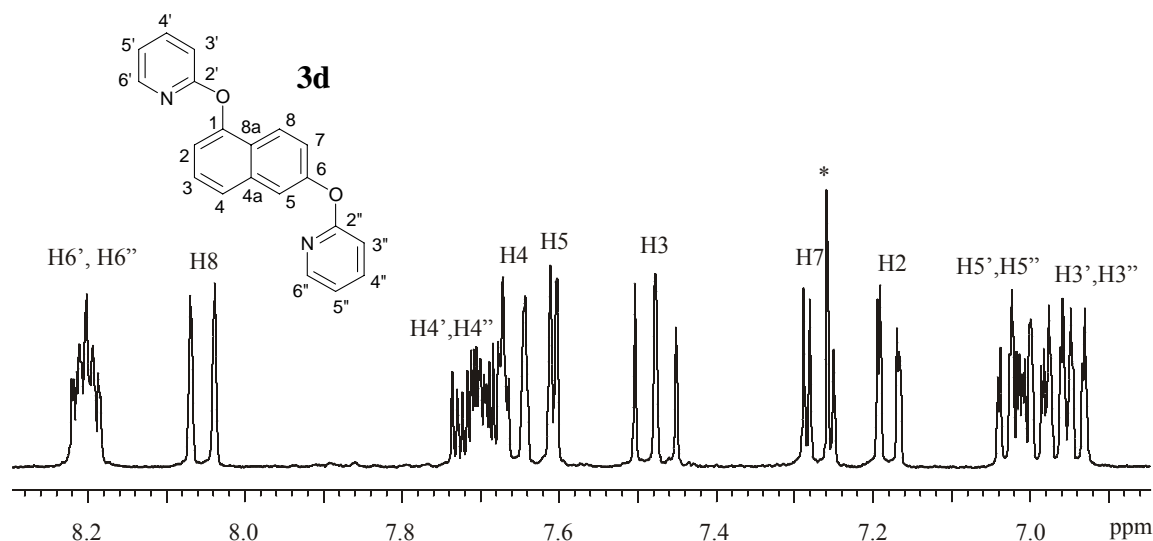
Disubstitution of a benzene core allows only three possible orientations (*ortho*, *meta* and *para*) of the appended heterocycles. In contrast, disubstitution of a naphthalene core leads to ten isomeric possibilities. Thus, in order to maintain greater control over the exact distance and relative orientations of the donor substituents, we have now extended this design strategy to the preparation of isomers of bis(2-pyridyloxy)naphthalene (**3**). We now report the synthesis and NMR characterisation of eight of the ten possible isomers of **3**.

## Results and Discussion

Initially, all ten isomers of **3** were viewed as targets for synthesis. Our previous syntheses of the three isomeric bis(2-pyridyloxy)benzenes [3,5] employed a solvent-free procedure for the nucleophilic aromatic substitution of 2-bromopyridine by the isomeric dihydroxybenzenes. This proved to be inefficient for the corresponding dihydroxynaphthalenes, thus various experimental conditions (solvent, base, temperature, reaction time) were explored in an effort to improve yields. No high yielding general procedure was found for these reactions, principally because of isolation problems of these somewhat irksome reaction products. In the end, two procedures (both using potassium carbonate as base) were found to be suitable and differed in the solvent employed (Scheme 1): method A was carried out in DMF, whilst method B used a sulpholane/toluene solvent mixture, which was based on a previously reported series of reactions of dihydroxynaphthalenes [6]. Two of the ten possible isomers proved to be inaccessible; the instability of 1,2-dihydroxynaphthalene prevented access to this isomer, and reaction of 1,8-dihydroxynaphthalene failed to produce any evidence of the desired product. In general the sulpholane/toluene procedure (method B) provided better yields (Table 1).



<b>Table 1.</b> Isolated yields for the various isomers of <b>3</b> .								
Isomer	1,3- ( <b>3a</b> )	1,4- ( <b>3b</b> )	1,5- ( <b>3c</b> )	1,6- ( <b>3d</b> )	1,7- ( <b>3e</b> )	2,3- ( <b>3f</b> )	2,6- ( <b>3g</b> )	2,7- ( <b>3h</b> )
Method A (%)	8	28	21	18	24	57	30	30
Method B (%)	24	-	-	29	67	-	75	37



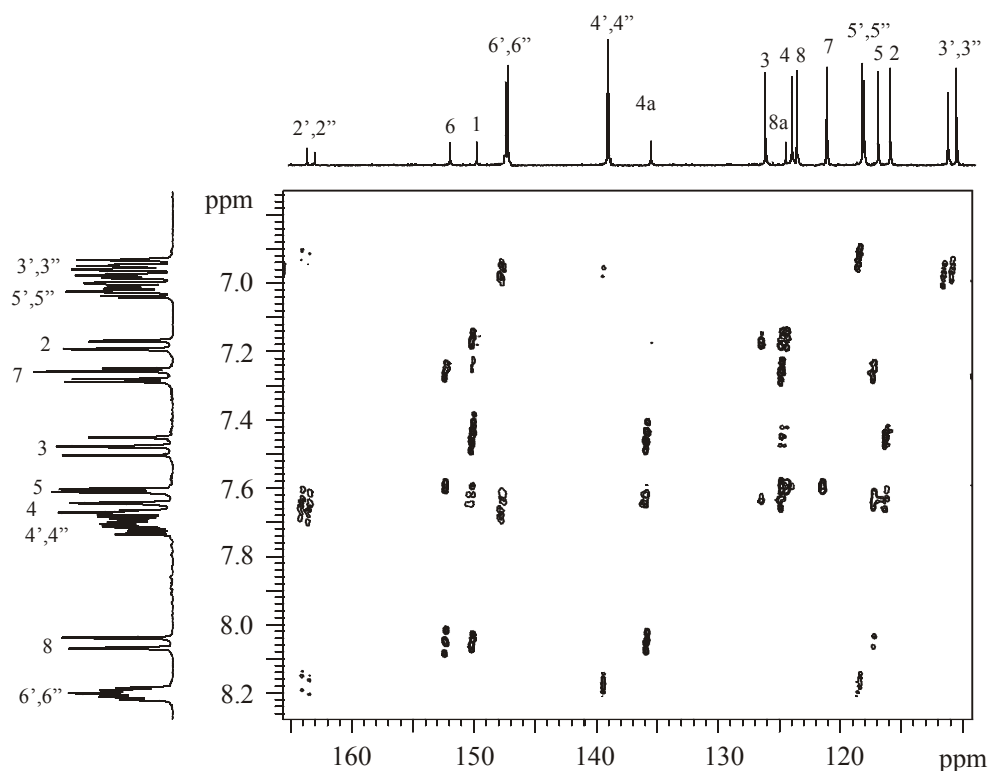
**Figure 1.**  $^1\text{H}$  NMR spectrum of **3d**. The peak marked with an asterisk is due to the solvent.

All eight isomers were fully characterised by elemental analysis and  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy. Complete assignment of the NMR spectra required a battery of 1- and 2-D techniques. As a representative example the spectra of 1,6-bis(2-pyridyloxy)naphthalene (**3d**) are discussed. Figure 1 shows the  $^1\text{H}$  NMR spectrum of **3d** which has fourteen non-equivalent aromatic protons. The assignments of some protons (e.g. H5 and H3) are immediately obvious from the spin-spin coupling patterns. The signals were readily grouped into the individual spin systems by means of 1D TOCSY experiments [7]. By incremental increase of the mixing times it was possible to readily identify the individual protons within each ring. This readily identified the signals for the two pyridine rings but did not allow distinction between the two overlapping sets of signals.

A subsequent 2D GHSQC spectrum allowed assignment of the protonated carbon signals. Finally, the signals for the non-protonated carbons were assigned by means of a 2D GHMBC spectrum (Figure 2). For example, the peak at 152.28 ppm correlates to H7, H5 ( $^2J_{\text{CH}}$ ) and H8 and therefore can be assigned to C6, whereas the peak at 150.08 ppm correlates to H2 ( $^2J_{\text{CH}}$ ), H7 ( $^4J_{\text{CH}}$ ), H3, H5 ( $^4J_{\text{CH}}$ ), and H8 and therefore can be assigned to C1. Similarly, distinction between C4a and C8a was made on the basis that the former shows correlations to H3, H4 ( $^2J_{\text{CH}}$ ) and H8, whereas the latter correlates to H2, H7, H3 ( $^4J_{\text{CH}}$ ), H5, and H4. The other correlations in this spectrum also served to confirm the earlier assignments of the other protons and carbons. The spectra of the other isomers were assigned by analogous methods.

These isomeric compounds were prepared for use as synthons in metallocsupramolecular chemistry, based on previous work with related bis-ethers [3-5,8,9] and bis-thioethers [10-16]. By varying the substitution pattern in the naphthalene ring system, it is expected to gain more subtle control of the

distances between metal centres bridged by these bidentate ligands. In the event, the 1,4-isomer **3b** proved to be unaccommodating, due to its insolubility in common reaction solvents, but the other isomers have been found to be functional reactants for the assembly of an intriguing array of metal complexes that will be reported in the near future. We have previously reported their use in regioselective double cyclopalladation reactions [17].



**Figure 2.** GHMBC spectrum of **3d**.

## Experimental Section

### General techniques

NMR spectra were recorded on a Varian 300 Unity spectrometer with a 3mm probe operating at 300 MHz and 75 MHz for  $^1\text{H}$  and  $^{13}\text{C}$ , respectively. Spectra were recorded in  $\text{CDCl}_3$  and referenced relative to internal  $\text{Me}_4\text{Si}$ . When required, nOe, 1-D TOCSY, GHSQC and GHMBC experiments were performed using standard pulse sequences and parameters available with the Unity 300 system. In the  $^1\text{H}$  NMR spectra listed below only  $^3J$  coupling constants are listed, which is useful for assignment purposes due to the following characteristic values [18] H3 (d,  $J = 8$  Hz), H4 (t,  $J = 8$  Hz), H5 (dd,  $J = 8, 5$  Hz), H6 (d,  $J = 5$  Hz).

Mass spectra were recorded using a Kratos MS80RFA spectrometer with a Mac 3 data system. Electron Impact spectra were obtained at 70eV with a source temperature of 150 °C.

Melting points were determined using an Electrothermal melting point apparatus and are uncorrected. Elemental analyses were performed by the Chemistry Department, University of Otago, Dunedin.

### General procedures for the preparation of the bis(2-pyridyloxy)naphthalenes

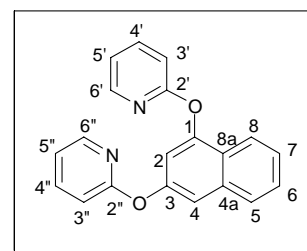
**Method A:** A mixture of the dihydroxynaphthalene (1 equiv.), 2-bromopyridine (3 equiv.) and potassium carbonate (4 equiv.) was refluxed in DMF for 72 hours. The mixture was added to a solution of aqueous sodium hydroxide (10%) and this was repeatedly extracted with chloroform. The chloroform was removed *in vacuo* and the resulting DMF solution was added to acetone. This solution was heated, treated with decolourising charcoal, then filtered. The solvent was then removed to give the crude product, which was purified by recrystallisation and/or column chromatography.

**Method B:** A mixture of the dihydroxynaphthalene (1 equiv.) and potassium carbonate (4 equiv.) was stirred in sulpholane/toluene (2:1) with nitrogen bubbling through it for 30 min. To this was added 2-bromopyridine (3 equiv.). The mixture was heated under nitrogen for 40 hours then added to a solution of aqueous sodium hydroxide (10%) and this was repeatedly extracted with chloroform. The chloroform was removed *in vacuo* and the resulting sulpholane solution was added to acetone. This solution was heated, treated with decolourising charcoal, then filtered. The acetone was removed *in vacuo* and water was added to the sulpholane solution to precipitate the crude product which was filtered off and redissolved with acetone. The product was allowed to crystallise from this solution.

#### 1,3-Bis(2-pyridyloxy)naphthalene **3a**

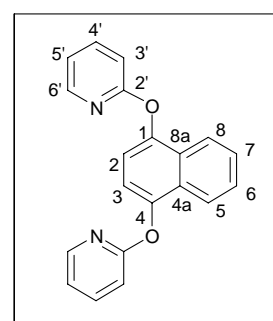
Method B. Reaction of 1,3-dihydroxynaphthalene (0.800 g, 4.99 mmol), 2-bromopyridine (1.63 g, 10.3 mmol), potassium carbonate (2.91 g, 21.1 mmol) in sulpholane/toluene gave crude **3a**, which was recrystallised from acetone/water to give **3a** as colourless crystals (0.391 g, 24%), m.p. 105–106 °C (Found: C, 76.46; H, 4.44 N, 9.04. C<sub>20</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub> requires C, 76.42; H, 4.49; N, 8.91. Found M<sup>+</sup>, 314.1047. C<sub>20</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub> requires M<sup>+</sup>, 314.1055).

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 6.94–7.02 (4H, m, H3', H3'', H5', H5''), 7.10 (1H, m, H2), 7.40 (1H, t, H7), 7.46 (1H, s, H4), 7.49 (1H, t, H6), 7.68 (2H, m, H4', H4''), 7.81 (1H, d, H5), 8.01 (1H, d, H8), 8.20 (2H, m, H6', H6''). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ: 111.17, 111.69, C3', C3''; 112.76, C2; 114.28, C4; 118.75, C5', C5''; 122.16, C8; 125.09, C8a; 125.30, C7; 127.07, C6; 127.56, C5; 135.02, C4a; 139.48, 139.56, C4', C4''; 147.80, 147.97, C6', C6''; 151.12, C1; 151.59, C3; 163.50, 163.90, C2', C2''.



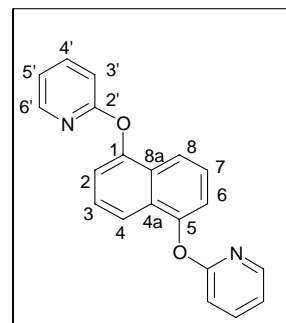
#### 1,4-Bis(2-pyridyloxy)naphthalene **3b**

Method A. A mixture of 1,4-dihydroxynaphthalene (1.10 g, 6.9 mmol), 2-bromopyridine (2.17 g, 13.7 mmol) and potassium carbonate (1.89 g, 13.7 mmol) was refluxed in DMF (10ml) for 22 hours. Removal of solvent and subsequent washing of the residue with water, then methanol gave **3b** (0.60 g, 28%), m.p. >130°C (dec.) (Found: C, 76.04; H, 4.18; N, 8.60). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 6.99 (2H, d, H3'), 7.01 (2H, t, H5'), 7.25 (2H, s, H2,3), 7.48 (2H, d, H6,7), 7.71 (2H, t, H4'), 8.01 (2H, d, H5,8), 8.19 (2H, d, H6'). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ: 110.88, C3'; 117.12, C2,3; 118.46, C5'; 122.32, C6,7; 126.63, C5,8; 128.56, C4a,8a; 139.57, C4'; 146.93, C1,4; 147.81, C6'; 164.28, C2'.



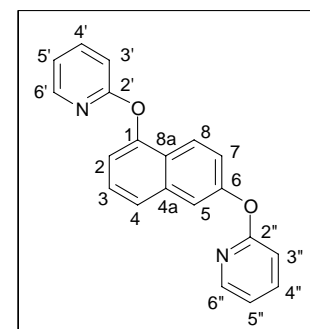
#### 1,5-Bis(2-pyridyloxy)naphthalene **3c**

Method A. Reaction of 1,5-dihydroxynaphthalene (1.10 g, 6.87 mmol), 2-bromopyridine (2.17 g, 13.7 mmol), potassium carbonate (1.90 g, 13.7 mmol) in DMF gave crude **3c**, which was recrystallised from acetone/water to give **3c** as pale yellow crystals (0.450 g, 21%), m.p. 187–188 °C (Found: C, 76.34; H, 4.42; N, 9.12. Found  $M^+$ , 314.1056).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 6.97 (2H, d, H3'), 7.02 (2H, t, H5'), 7.26 (2H, d, H2, H6), 7.45 (2H, t, H3, H7), 7.71 (2H, t, H4'), 7.90 (2H, d, H4, H8), 8.20 (2H, d, H6').  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 111.07, C3'; 117.67, C2, C6; 118.55, C5'; 119.13, C4, C8; 126.01, C3, C7; 129.15, C4a, C8a; 139.53, C4'; 147.94, C6'; 150.19, C1, C5; 164.21, C2'.



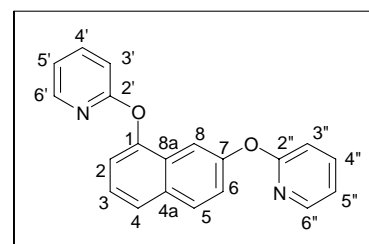
#### 1,6-Bis(2-pyridyloxy)naphthalene **3d**

Method A. Reaction of 1,6-dihydroxynaphthalene (1.10 g, 6.87 mmol), 2-bromopyridine (2.17 g, 13.7 mmol), potassium carbonate (3.80 g, 27.5 mmol) in DMF gave crude **3d**, which was purified by column chromatography and recrystallisation from acetone/water to give **3d** as pale yellow crystals (0.387 g, 18%), m.p. 101–102 °C (Found: C, 76.21; H, 4.50; N, 8.92. Found  $M^+$ , 314.1059).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 6.93 (2H, m, H3', H3''), 6.97 (2H, m, H5', H5''), 7.18 (1H, d, H2), 7.27 (1H, d, H7), 7.48 (1H, t, H3), 7.61 (1H, s, H5), 7.67 (1H, d, H4), 7.71 (2H, m, H4', H4''), 8.05 (1H, d, H8), 8.20 (2H, m, H6', H6'').  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 110.82, 111.50, C3', C3''; 116.24, C2; 117.24, C5; 118.39, 118.53, C5', C5''; 121.40, C7; 123.86, C8; 124.27, C4; 124.78, C8a; 126.45, C3; 135.81, C4a; 139.36 (2C), C4', C4''; 147.53, 147.73, C6', C6''; 150.08, C1; 152.28, C6; 163.36, 163.99, C2', C2''.



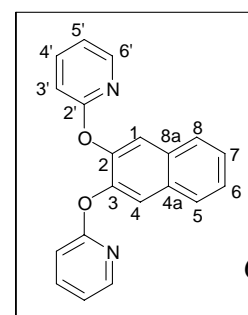
#### 1,7-Bis(2-pyridyloxy)naphthalene **3e**

Method B. Reaction of 1,7-dihydroxynaphthalene (1.13 g, 7.05 mmol), 2-bromopyridine (2.23 g, 14.1 mmol), potassium carbonate (3.93 g, 28.4 mmol) in sulpholane/toluene gave crude **3e**, which was recrystallised from acetone/water to give **3e** as colourless crystals (1.48 g, 67%), m.p. 118–119 °C (Found: C, 76.34; H, 4.28; N, 8.86. Found  $M^+$ , 314.1056).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 6.90 (2H, m, H3', H3''), 6.98 (2H, m, H5', H5''), 7.25 (1H, d, H2), 7.33 (1H, d, H6), 7.45 (1H, t, H3), 7.66 (2H, m, H4', H4''), 7.71 (1H, s, H8), 7.72 (1H, d, H4), 7.92 (1H, d, H5), 8.16 (2H, m, H6', H6'').  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 110.99, 111.40, C3', C3''; 112.15, C8; 117.56, C2; 118.46, 118.51, C5', C5''; 122.01, C6; 124.72, C4; 125.03, C3; 128.40, C8a; 129.71, C5; 132.47, C4a; 139.35, 139.44, C4', C4''; 147.68, 147.84, C6', C6''; 149.66, C1; 152.10, C7; 163.61, 164.04, C2', C2''.



#### 2,3-Bis(2-pyridyloxy)naphthalene, **3f**

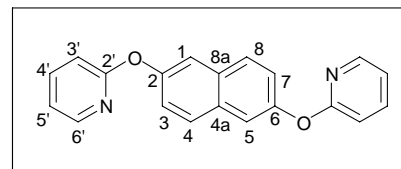
Method A. Reaction of 2,3-dihydroxynaphthalene (1.10 g, 6.87 mmol), 2-bromopyridine (2.17 g, 13.7 mmol), potassium carbonate (3.80 g, 27.5 mmol) in DMF gave crude **3f**, which was recrystallised from acetone/water to give **3f** as



colourless crystals (1.22 g, 57%), m.p. 161-162 °C (Found: C, 76.25; H, 4.42; N, 8.84. Found  $M^+$ , 314.1051).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 6.72 (2H, d, H3'), 6.93 (2H, t, H5'), 7.45 (2H, m, H6, H7), 7.58 (2H, t, H4'), 7.72 (2H, s, H1,4), 7.80 (2H, m, H5, H8), 8.11 (2H, d, H6').  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 110.84, C3'; 118.36, C5'; 120.50, C1, C4; 125.63, C6, C7; 127.29, C5, C8; 131.58, C4a, C8a; 139.06, C4'; 144.98, C2, C3; 147.39, C6'; 163.25, C2'.

### 2,6-Bis(2-pyridyloxy)naphthalene **3g**

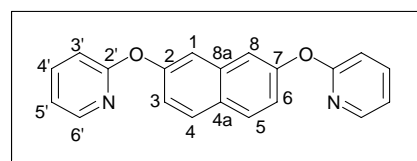
Method B. Reaction of 2,6-dihydroxynaphthalene (0.795 g, 4.96 mmol), 2-bromopyridine (2.35 g, 14.9 mmol), potassium carbonate (2.93 g, 21.2 mmol) in sulpholane/toluene gave crude **3g**, which was purified by recrystallisation from acetone/water to give **3g** as pale yellow-brown crystals (1.18 g, 75%), m.p. 146-147 °C (Found:



C, 76.71; H, 4.53; N, 9.16. Found  $M^+$ , 314.1055).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 6.95 (2H, d, H3'), 7.02 (2H, t, H5'), 7.31 (2H, d, H3, H7), 7.59 (2H s, H1, H5), 7.71 (2H, t, H4'), 7.82 (2H, d, H4, H8), 8.21 (2H, d, H6').  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 111.46, C3'; 117.60, C1, C5; 118.51, C5'; 122.04, C3, C7; 129.06, C4,8; 131.70, C4a, C8a; 139.42, C4'; 147.76, C6'; 151.37, C2, C6; 163.83, C2'.

### 2,7-Bis(2-pyridyloxy)naphthalene **3h**

Method A. Reaction of 2,7-dihydroxynaphthalene (1.10 g, 6.87 mmol), 2-bromopyridine (2.17 g, 13.7 mmol), potassium carbonate (3.80 g, 27.5 mmol) in DMF gave crude **3h**, which was purified by column chromatography and recrystallisation from acetone/water to give **3h** as pale yellow crystals (0.658 g, 30%), m.p. 112-113 °C



(Found: C, 76.49; H, 4.24; N, 8.77. Found  $M^+$ , 314.1053).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 6.95 (2H, d, H3'), 7.02 (2H, t, H5'), 7.26 (2H, d, H3, H6), 7.50 (2H, s, H1, H8), 7.70 (2H, t, H4'), 7.88 (2H, d, H4, H5), 8.21 (2H, d, H6').  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 111.62, C3'; 117.03, C1, C8; 118.62, C5'; 120.64, C3, C6; 128.44, C4a; 129.53, C4, C5; 135.26, C8a; 139.45, C4'; 147.82, C6'; 152.49, C2, C7; 163.72.

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*Sample Availability:* Contact the authors.